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(54) **A seal assembly with new resin stabilized adhesive composition to bond an insert member to the elastomeric seal material**

(57) In a seal assembly having a support member made of either metal or plastic, and an elastomeric sealing material bonded by an adhesive composition to said support member, said composition being an epoxy resin stabilized silane adhesive composition made up from the following materials in parts by volume, (a) 1 to 80 parts organosilane material, which also includes a silane coupling agent, and a hydrolyzing agent for the

organosilane, (b) 0.5 to 70 parts epoxy resin material, which includes an amine curing agent for the epoxy resin, (c) 50 to 3000 parts of aqueous fluid carrier medium for the composition, (d) 0.05 to 20 parts of additive material selected from the group consisting of a surfactant material and a rust inhibitor material.

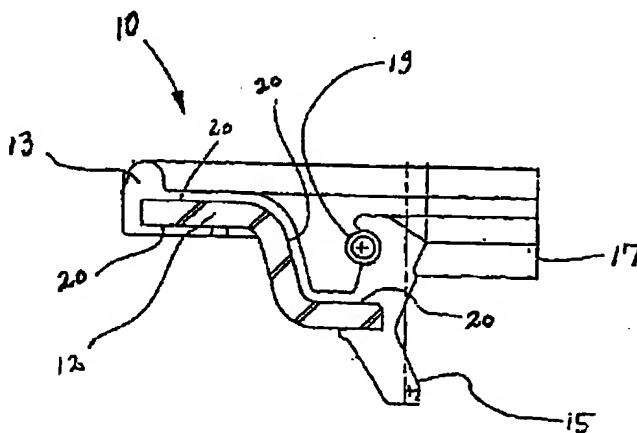


FIG. 1

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**Description****Background Of The Invention**

- 5 [0001] This invention broadly relates to a new seal assembly wherein a novel resin stabilized adhesive composition is used for bonding the rubber or elastomeric seal material to a metal or plastic insert member.
- [0002] This application is a continuation of U.S. provisional Application Serial No. 60/079,032, filed March 23, 1998.
- [0003] The state of the prior art is indicated by the following cited references, U.S. Patent Nos.: 3,869,340; 3,887,602; 4,052,524; 4,246,145; 4,323,488; 5,470,662; and 5,633,038.
- 10 [0004] In the past it has been known to adhesively bond insert members, such as inserts made of either metal or plastic, to a rubber or elastomer sealing material using various types of bonding adhesives. Previous aqueous organosilane adhesives tended to be very unstable and sensitive to changes in pH, temperature, and other environmental conditions. Such organosilane adhesives also provided little environmental resistance and therefore tended to de-bond or separate under numerous commonly encountered environmental conditions. Another problem with the past silane adhesives is
- 15 their inability to build adequate film thickness for many required applications.

**Summary Of The Invention**

- [0005] It has been unexpectedly discovered, in accordance with this invention, that through the use of water dispers-  
 20 able epoxy resins in formulating the adhesives composition of this invention that there has been obtained greatly improved stability and environmental resistance, and adhesive film build-up is also significantly improved. It has also been discovered that the past stability has been increased by approximately 30 times, through the use of the inventive techniques disclosed herein. The film build-up characteristics of the previously known silane adhesives has been increased by a factor of approximately five times. Also it has been found that through the use of the invention described  
 25 herein the environmental resistance is greatly improved.

**Brief Description Of The Drawing****[0006]**

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Figure 1 shows a seal assembly in accordance with the invention.

**Description of Preferred Embodiments And Best Mode**

- 35 [0007] A seal assembly in accordance with the invention is illustrated Figure 1. The seal assembly designated 10 is comprised of a metal or plastic insert 12 which has molded therearound a rubber or elastomeric material 13. The seal assembly is shown in one-quarter sectional view as will be appreciated by those skilled in the art. The rubber or elastomeric material 13 also includes a portion thereof normally referred to as the sealing lip 15 and the excluder seal portion 17. Behind the excluder seal portion there is frequently placed a garter spring or elastic retainer member  
 40 designated 19 which acts to press or secure the seal portion 17 against a circular member such as a piston, axle or strut (not shown) which is being sealed off. The surface designated 20 on the insert 12 is the entire surface of the insert which is in contact with the rubber or elastomeric material 13 therearound.
- [0008] This surface portion 20 of the insert 12 is adhered to the elastomeric material 13 through the use of a unique epoxy resin stabilized silane adhesive composition. This epoxy resin stabilized silane adhesive composition, in accordance with the discovery of this invention, comprises and is made up of the following materials in parts by volume: (a) 1  
 45 to 80 parts organosilane adhesive material, which also includes a silane coupling agent, and a hydrolyzing agent for the organosilane, (b) 0.5 to 70 parts epoxy resin material, which includes an amine curing agent for the epoxy resin, (c) 50 to 3000 parts of aqueous fluid carrier medium for the composition, (d) 0.05 to 20 parts of additive material selected from the group consisting of a surfactant material and a rust inhibitor material. More preferably, the composition of the epoxy  
 50 resin stabilized silane adhesive composition should be as follows: component (a) is between 2 and 60 parts, component (b) is between 1 and 55 parts, component (c) is between 60 and 1000 parts, and component (d) is between 0.1 and 10 parts. Best results are obtained when: component (a) is between 3 and 20 parts, component (b) is between 2 and 15 parts, component (c) is between 100 and 700 parts, and component (d) is between 0.2 and 8 parts.
- [0009] The epoxy resin stabilized silane adhesive composition is applied to the metal insert (or in some cases it may  
 55 be a plastic insert) of the seal assembly 10 on the surface thereof designated 20 at a thickness of approximately 0.05 mils, and the adhesive is then dried with hot air (for about 15 minutes at about 300°F). The rubber seal is subsequently molded over the insert, and the adhesive is cured at the same time that the rubber (or elastomeric material) is cured and set up on the insert 12.

[0010] In order to further illustrate the invention, the following examples are provided; however, they are not intended to be limiting on the scope of the invention as set forth in the subjoined claims.

### Example 1

[0011]

Phosphatizer Apparatus Used = 750 gallons size $\approx$ 2850 Liters	
Ingredients	Description
Tergitol NP-6	[Surfactant, Non-ionic, Nonyphenol Polyethylene Glycol Ether] ~ 97% - Nonyphenol Ethoxylate ~ 1.5% - Polyethylene Glycol ~ 1.5% - Dinonylphenol Ethoxylate
Si-264	- Organosilane, 3-Thiocyanatopropyltriethoxysilane $(C_2H_5O)_3 Si-(CH_2)_3-SCN$ (available from DeGussa Co.)
A1100	- Silane Coupling Agent, 3-Aminapropyltriethoxysilane (O.S.I. Co.)
Z6020	- Silane Coupling Agent, 3-(Z-Aminoethylamino)propyltrimethoxysilane (Dow Corning Co.)
Acetic Acid	- $CH_3COOH$ (hydrolyzing agent for the organosilane)
CF Rinse	- Rust Inhibitor

### MIXING INSTRUCTIONS

Added:	~2795L of Water (L = liter) .85L of Tergitol 7L of Acetic Acid 25.5L of Si264
Agitate for 24 hours	
Check pH: (3.0-3.3)	Actual = 3.2
Added:	4L of A1100 4L of Z6020
Agitate for 2 hours	
Added:	14L of CF Rinse
Check pH: (4.0-4.5)	Actual = 4.4

[0012] Ran parts through the phosphatizer

P/N	Compound	Initial Bond Results; R/R Tear
33394	A0706	100

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(continued)

P/N	Compound	Initial Bond Results; R/R Tear
35866	A0806	100
35125	K0707	100
37613	P0814	100

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10 [0013] The adhesive is applied to the metal insert (or in some cases plastic insert) of the seal assembly at a thickness of about 0.05 mils, and the adhesive is then dried with hot air (15 min. at 300°F). The rubber seal is subsequently molded over the insert, and the adhesive is cured at the same time that the rubber (or elastomeric material) is cured and set upon the insert.

[0014] Shelf life of treated cases was performed on P/N 35866

15 The bond was good for 21 days.

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Example 2

[0015]

IngredientsDescription

Same Ingredients as in Ex. No. 1 plus the following:--

EPI-REZ 3515-260	Waterborne Resin, Nonionic, Aqueous Dispersion of a bisphenol A epoxy resin (Shell Oil Co.)
EPI-REZ 3510-W-60	Waterborne Resin, Nonionic, Aqueous Dispersion of A bisphenol A epoxy resin (Shell Oil Co.)
EPI-CURE 3055	Aliphatic Amidoamine Curing Agent (Shell Oil Co.)
EPI-CURE 3253	Tertiary Amine Curing Agent (Shell Oil Co.)

Determination of the effectiveness of the resins on the stability of the Adhesive; mixed 3 lab Batches.

LAB BATCH 1: No Resin or Curative

LAB BATCH 2: 3510 Resin &amp; 3253 Curative

LAB BATCH 3: 3515 Resin &amp; 3055 Curative

The mixing procedure was as follows:

		Amount (ml)		
Mix while agitating:		1	2	3
Water		483	478	478
1/2 of Curative		0	.5	.5
Tergitol (surfactant)		.2	.2	.2
Acetic Acid (hydrolyzing agent)		2.4	2.4	2.4
Si264 (organosilane)		4	4	4
Agitate 4 hours				
Add:	Resin	0	2.5	2.5
Agitate for 20 hours				
Check pH: should be 3.0 - 3.3				
Add:	A1100 (silane coupling agent)	4	4	4
	Z6020 (silane coupling agent)	4	4	4
Agitate 2 hours				
Add:	CF Rinse (rust inhibitor)	2.5	2.5	2.5

Example 3

[0016]

## Resin Stabilized Waterborne Silane Adhesive

IngredientsDescription

Same ingredients as in Examples 1 & 2; plus the following:--

Ultraseal (Oakite Co.)	Rust Inhibitor containing water, A1100, and Titanium Chelate
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Goal of this batch was to hold stability; also to bond all of the current Neptune (Waterborne Silane Adhesive) only jobs; also to bond a wide range of NBR compounds. Also the Resin should provide the adhesive a better range of compounds.

Mixing ProcedureAmount (ml)

Add while agitating mildly

300 ml H<sub>2</sub>O  
 .5 ml Tergitol  
 1.5 ml Acetic Acid  
 3.0 ml Si264

Agitate for 4 hours  
 Then add:

6.0 ml 3515  
 6.0 ml 3510  
 2.2 ml A1100  
 2.8 ml Z6020  
 15 ml Ultraseal  
 1.7 ml CF Rinse

Check pH: 3.9 Added 2 ml Acetic Acid  
 pH: 3.1 - o.k.

Agitate for 24 hours  
 Then add:

1.5 ml 3055  
 1.5 ml 3253

Agitated for 24 hours (4 hours should  
 be sufficient)

Check pH: 4.35 o.k.

Treated panels with the adhesive and molded bond panels.

**Example 4**

[0017]

Resin-Stabilized Silane Adhesive	
See ingredients listed on pages 154, 011 - 015.	
Mixing Procedure	Amount (ml)
Mix while agitating mildly:	295 ml H <sub>2</sub> O .5 ml Tergitol 1.5 ml Acetic Acid 3.75 ml Si264
pH = 2.5	
Mix separately: Silane Mixture	2.5 ml A1100 3.5 ml Z6020 6 ml H <sub>2</sub> O
Agitate for 4 hours	
Add while agitating:	10.0 ml 3515 10.0 ml 3510 12.0 Silane Mixture 15 ml Ultraseal 2 ml CF Rinse
Agitate for 4 hours	
pH = 4.15	
Agitate 20 hours &	
Add while agitating:	4 ml 3055 1 ml 3253
Agitate 15 mins.	
pH = 4.2	

[0018] While it will be apparent that the preferred embodiments of the invention disclosed are well calculated to fulfill the objects, benefits, or advantages of the invention, it will be appreciated that the invention is susceptible to modification, variation, and change without departing from the proper scope or fair meaning of the subjoined claims.

**Claims**

1. In a seal assembly having a support member made of either metal or plastic, and an elastomeric sealing material bonded by an adhesive composition to said support member, said composition being an epoxy resin stabilized silane adhesive composition made up from the following materials in parts by volume,

(a) 1 to 80 parts organosilane material, which also includes a silane coupling agent, and a hydrolyzing agent for the organosilane,

(b) 0.5 to 70 parts epoxy resin material, which includes an amine curing agent for the epoxy resin,

(c) 50 to 3000 parts of aqueous fluid carrier medium for the composition,

(d) 0.05 to 20 parts of additive material selected from the group consisting of a surfactant material and a rust inhibitor material.

2. The invention of claim 1 wherein,

component (a) is between 2 and 60 parts,

component (b) is between 1 and 55 parts,

component (c) is between 60 and 1000 parts, and

component (d) is between 0.1 and 10 parts.

3. The invention of claim 1 wherein,

component (a) is between 3 and 20 parts,

component (b) is between 2 and 15 parts,

component (c) is between 100 and 700 parts, and

component (d) is between 0.2 and 8 parts.

4. An epoxy resin stabilized silane adhesive composition, comprising and made up of the following materials in parts by volume,

(a) 1 to 80 parts organosilane adhesive material, which also includes a silane coupling agent, and a hydrolyzing agent for the organosilane,

(b) 0.5 to 70 parts epoxy resin material, which includes an amine curing agent for the epoxy resin,

(c) 50 to 3000 parts of aqueous fluid carrier medium for the composition,

(d) 0.05 to 20 parts of additive material selected from the group consisting of a surfactant material and a rust inhibitor material.

5. The invention of claim 4 wherein,

component (a) is between 2 and 60 parts,

component (b) is between 1 and 55 parts,

component (c) is between 60 and 1000 parts, and

component (d) is between 0.1 and 10 parts.

6. The invention of claim 1 wherein,

component (a) is between 3 and 20 parts,

component (b) is between 2 and 15 parts,

component (c) is between 100 and 700 parts, and

component (d) is between 0.2 and 8 parts.

7. A seal assembly having a support member made of either metal or plastic, and an elastomeric sealing material bonded by an adhesive composition to said support member, said composition being an epoxy resin stabilized

silane adhesive composition comprising in parts by volume,

(a) 1 to 80 parts organosilane adhesive material, which also includes a silane coupling agent, and a hydrolyzing agent for the organosilane,

(b) 0.5 to 70 parts epoxy resin material, which includes an amine curing agent for the epoxy resin,

(c) 50 to 3000 parts of aqueous fluid carrier medium for the composition,

(d) 0.05 to 20 parts of additive material selected from the group consisting of a surfactant material and a rust inhibitor material.

8. The invention of claim 7 wherein,

component (a) is between 2 and 60 parts,

component (b) is between 1 and 55 parts,

component (c) is between 60 and 1000 parts, and

component (d) is between 0.1 and 10 parts.

9. The invention of claim 7 wherein,

component (a) is between 3 and 20 parts,

component (b) is between 2 and 15 parts,

component (c) is between 100 and 700 parts, and

component (d) is between 0.2 and 8 parts.

10. The invention of claim 7 wherein,

said seal assembly uses a metal insert, which has a surface portion thereof in contact with the elastomeric sealing material.

11. The invention of claim 10 wherein,

said elastomeric sealing material is rubber.

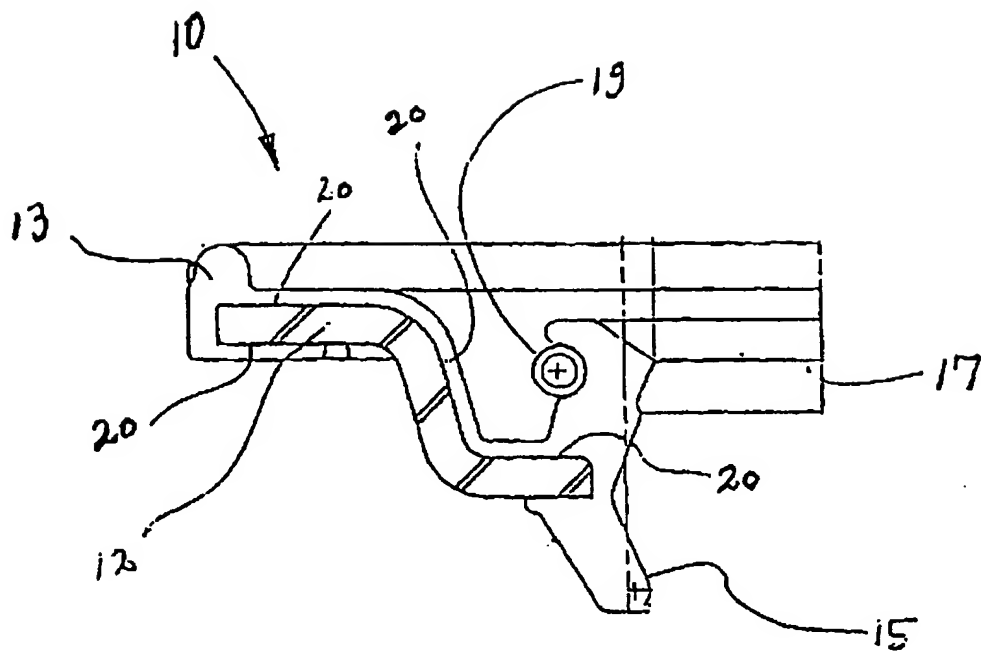


FIG. 1



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# EUROPEAN SEARCH REPORT

Application Number  
EP 99 10 5736

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.8)
A	US 5 714 532 A (CHEN MING J ET AL) 3 February 1998 * the whole document *	1-11	C09J163/00 F16J15/00 C09K3/10 C09J183/04
A	DE 195 00 779 A (HENKEL KGAA) 18 July 1996 * the whole document *	4,5	
			TECHNICAL FIELDS SEARCHED (Int.Cl.8)
			C09J F16J C09K
The present search report has been drawn up for all claims			
Place of search <b>MUNICH</b>		Date of completion of the search <b>29 June 1999</b>	Examiner <b>olde Scheper, B</b>
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 99 10 5736

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5714532 A	03-02-1998	WO 9814511 A EP 0868476 A	09-04-1998 07-10-1998
DE 19500779 A	18-07-1996	WO 9621632 A	18-07-1996

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